Solid State Electrolytes Prepared from PEO(360) Silanated Silica

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Abstract

All solid state composite electrolytes were prepared using fumed silica (SiO_2) silanated with an oligomeric polyethylene oxide silane containing 6-9 ethylene oxide repeat units, a PEO matrix and $LiClO_4$ (8/1 O/Li). The PEO-silane covalently attached to the silica was amorphous, with a T_g that increased from $-90°C$ to $-53°C$ after attachment. The conductivity of films prepared using the PEO-silanated silica increased to ~ 6×10^{-5} S/cm at RT compared with ~1×10^{-5} S/cm for films prepared with unsilanated SiO_2.

Introduction

All solid state electrolytes (SSEs) that can be laminated to the electrodes in Li metal or Li ion rechargeable batteries are expected to improve their cycle and shelf-life. Polyethylene oxide (PEO) can be used as a SSE above its melt temperature of ~70°C, but crystallization of the polymer decreases its room temperature (RT) conductivity to ~10^{-7}S/cm. Composite polymer electrolytes prepared from inorganic fillers and PEO show improved mechanical and temperature stability[6,8] and enhanced RT conductivity[18]. Recently, composites of PEO with micron and nanometer sized ceramic particles such as SiO_2, Al_2O_3, or TiO_2 have been shown to have RT conductivities of 10^{-5} S/cm[5,7], predominantly as a result of the inhibition of the PEO crystallization[2,9], since in these systems, Li ion transport is believed to occur in the amorphous phase. The high surface area of the nano-size particles are most effective at inhibition of crystallization. However, recrystallization of the PEO occurs with time, resulting in lower ionic conductivity. A similar inhibition of crystallization is observed in PEO intercalated in nanoscale layered silicates[16]. Inorganic particles have also been shown to improve the stability of the electrode interface[1,3].

In PEO electrolytes, the transport of the Li ion is thought to occur through a "hopping" mechanism between vacant sites. Since increased free volume (V_f) should increase the number of these sites, ionic transport is expected to increase with V_f. One way of introducing free volume into polymers is to increase the number of chains ends, i.e. to decrease the molar mass or introduce branching[12]. This effect has been utilized in systems in which low molar mass PEO side chains have been attached to inorganic and organic polymer scaffolds[13]. The conductivity of comb-shaped high molecular weight PEO was observed to increase with increased content of tri(oxyethylene) side chains[10]. For pendant PEO groups, those with $n \sim 5-6$ ethylene oxide units, under equivalent conditions, have exhibited the highest conductivities[4,14].

In the present work, low molar mass PEO, with a number average molecular weight of ~360g/mol [referred to as PEO(360)] has been attached to fumed silica [referred to as PEO(360)-SiO_2] and incorporated in composite SPEs prepared from PEO [M_w = 600,000, or a 50/50 mixture of M_w= 600,000 and 1000] or combinations of PEO and a copolymer of polyvinylidene fluoride with hexafluoroisopropanol (PVDF-HFP). Comparative conductivity (σ) studies between PEO(360)-SiO_2 and pure SiO_2 blended with PEO indicate that σ increases with increasing weight fraction of low molar mass PEO, with the greatest effect arising from composites prepared from PEO(360)-SiO_2. A σ of ~ 6×10^{-5} S/cm at RT was obtained for composites prepared from the silanated silica.

Experimental
Aerosil 380 (A380) fumed silica, with a nominal diameter of 7nm and surface area of $380m^2/g$, was

obtained from deGussa. Attachment of the PEO was achieved by a silanization reaction using 2-[methoxy (polyethyleneoxy) propyl] trimethoxy silane (Gelest), shown in Figure 1. The nominal MW is from 458 (n=6) to 590 (n=9), but the MW of the PEO segment ranges from 295 (n=6) to 427 (n=9), with an average of 360 [referred to as PEO(360)-silane]. PEO(500) and PEO(350) were obtained from Aldrich.
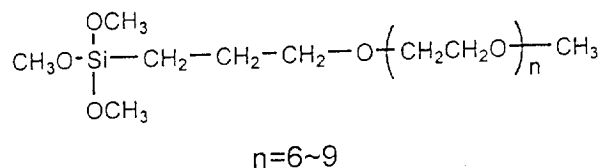

$$n=6\sim9$$

Figure1. PEO(360)-silane

The PEO(360)-SiO$_2$ was characterized by thermogravimetric analyis (TGA), using TA Instruments Hi-Res TGA2950 Thermogravimetric Analyzer, and differential scanning calorimetry (DSC), using a DSC 2920, both at scan rates of 10°C/min and under N$_2$ atmosphere. Ionic conductivity was measured from the complex impedance spectra obtained using a Schlumberger HF Frequency Response Analyzer (model SI 1255) in combination with an EG&G Princeton Applied Research (PAR model 273A) potentiostat/galvanostat in the frequency range from 0.01 to 100kHz, using stainless steel blocking electrodes.

A typical silanization reaction was carried out by first dispersing, for 1h with stirring, 3g of A380 in 250g hexane, followed by addition of 13g PEO(360)-silane; this mixture was stirred at RT for ~16h. The silanated silica settled to the bottom, and the supernate was decanted. The silanated silica was evacuated at RT under reduced pressure overnight, followed by evacuation in a vacuum oven at 90°C overnight. These procedures were adopted to increase the amount of covalently attached silane. In order to remove noncovalently bonded silane, the silanated silica was redispersed in methanol, centrifuged at ~3500rpm for ~1h, and the supernate decanted. This process was repeated 3x, followed by evacuation at RT. The amount of grafted PEO(360)-silane, determined by the TGA weight loss between 25 to 800°C, was

typically 28-34%. The proposed structure, shown in Figure 2, contains linkages both to the silica surface (via silanol groups) and between adjacent silane molecules.
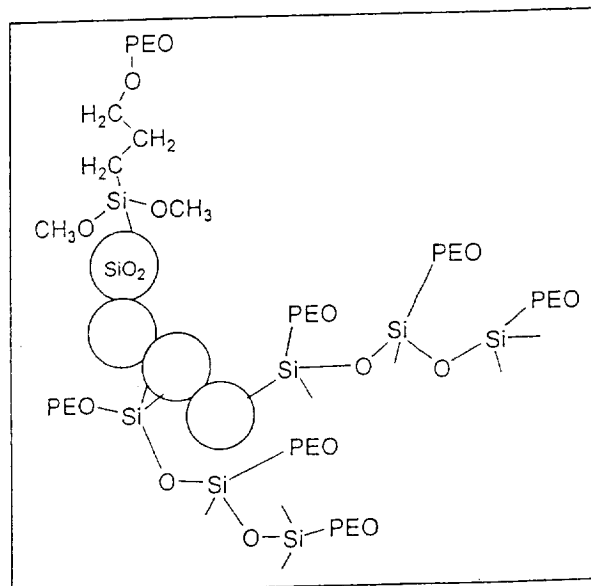

Figure 2. Structure of PEO(360)-SiO$_2$

Films were prepared in a dry glove box purged with argon by dispersing SiO$_2$ or PEO(360)-SiO$_2$ and LiClO$_4$ in acetonitrile, followed by addition of PEO. All materials were dried in a vacuum oven for ~24h [PEO at 55°C, LiClO$_4$ at 120°C, SiO$_2$ at 200°C, and PEO(360)-SiO$_2$ at 80°C] prior to preparation of the films. The O/Li ratio was 8/1. Films prepared using PEO(600,000)/ PEO(1000) in a 50/50 wt ratio were cast onto stainless steel film, and the others onto Teflon.

Results and Discussion

DSC traces, shown in Figure 3, of PEO(350) or PEO(500), not shown, are completely crystalline, and exhibit no glass transition temperature, T$_g$. PEO(360)-silane is semicrystalline, and exhibits a T$_g$ at −89.9°C. When physically adsorbed PEO(360)-silane is attached to fumed silica (i.e. before the heat treatment and rinsing steps), a semicrystalline material with a T$_g$ of −79°C is observed. After the heating and rinsing procedures, which leave only the covalently attached silane, there is almost no crystallization, and the T$_g$ increases to −53.3°C. Thus grafting of the silane onto the silica surface results in an

almost complete suppression of the crystallization and an increase in the glass transition temperature of ~35°C. Even in the case of physically adsorbed silane, there is an increase of 10°C in the T_g compared with the original material.
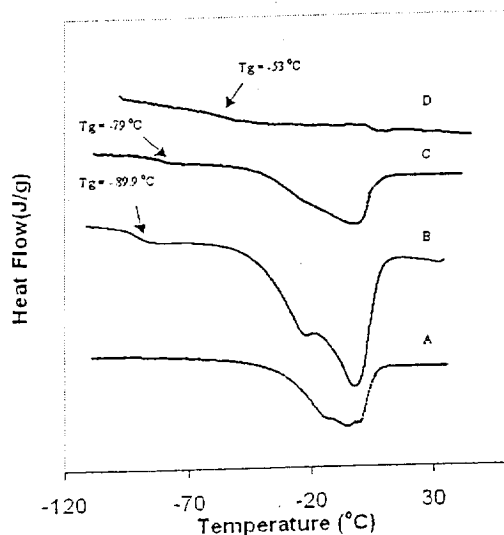

Figure 3: DSC traces of (A) PEO(350); (B) PEO(360)-silane; (C) physically adsorbed PEO(360)-silane; (D) grafted PEO(360)-SiO₂

Increases in T_g as a function of Al_2O_3 filler loading have previously been observed for polyether based composite electrolytes[17]. However, unlike the case of physically mixed high molecular weight PEO, Li salt composites, the suppression of crystallization for the grafted PEO(460)-silane, even in the absence of salt, is thermodynamically stable. Other investigators have observed an absence of crystallization of PEO side chains for chains with $M_n < 450$ (n~10) in the case of poly(ethylene oxide)-polyacrylates and polymethacrylates [19], and for n < 5 in the case of polyepoxides[14].

In order to investigate the effects of free volume on conductivity, films were prepared with increasing amounts of low molar mass but solid (at RT) PEO. Table I presents the composition (wt%) of PEO in the films. In all cases the amount of SiO_2 was 10%. The amount of the PEO(360) from the PEO(360)-silane was determined from TGA weight loss data.

Table I* Composition of PEO in films

Film	%PEO (360)	%PEO (600,000)	%PEO (1000)
1	0	90	0
2	0	45	45
3	3.8	86.2	0

*Films also contain 10% SiO_2 and $LiClO_4$ at 8/1 O/Li ratio

DSC traces for the dry films, after annealing at 100°C for 48h, exhibited no melt endotherms and had T_gs of −18°C. This value is higher than that reported in the literature[11], suggesting that the films are at least as dry as those prepared in other laboratories. Upon exposure to atmospheric moisture, T_g decreased.
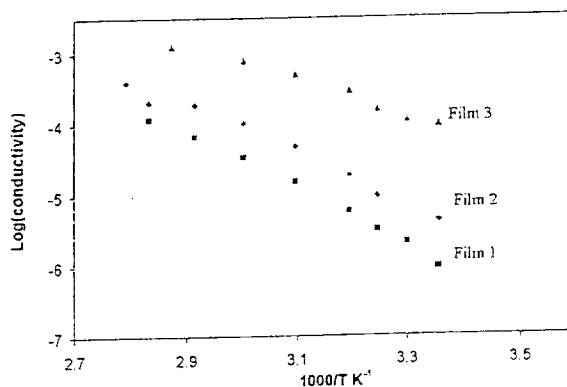

Figure 4. Temperature dependence of conductivity of films from Table I.

Figure 4 shows the temperature dependent conductivity data for films 1 and 2. There is a small increase in conductivity when low molar mass PEO (1000) is added to the PEO matrix. When 13.8% PEO(360)-silanated silica is added to PEO(600,000), film 3, the conductivity increases by at least a factor of 5 compared with film 1, although the amount of low molecular weight PEO(360) is considerably less than that achieved by addition of PEO(1000). Although the number of chain ends is approximately 3x greater for PEO(360) compared with the same weight percent PEO(1000), this cannot account for the difference in σ between films (2) and (3). Przyluski et al [15] have suggested a model in which the increase in conductivity in composite electrolytes compared

with polyether based electrolytes was due to the formation of highly conductive layers at the polyether matrix-filler interface. In addition, PEO segments of n $\sim$ 6 have been most effective in enhancing Li ion transport.

The films prepared using PEO(360)-silanated silica and PEO(600,000) were strong and self-supporting. Preliminary data for films prepared with PVDF-HFP, PEO(360)-SiO$_2$, PEO and LiClO$_4$ indicate that they are tougher, but that the conductvities are only reasonable if the total wt% of inert material (i.e. SiO$_2$ and PVDF-HFP) is less than $\sim$ 30%. Further work is in progress to improve both the conductivity and mechanical properties of the films.

Conclusions

Films prepared using PEO(360)-silanated silica, LiClO$_4$ and a PEO matrix exhibited conductivities of $\sim$6x10^{-5} at RT. Reasonable mechanical properties were obtained from processable films without the necessity of forming a crosslinked network.

Acknowledgements

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